

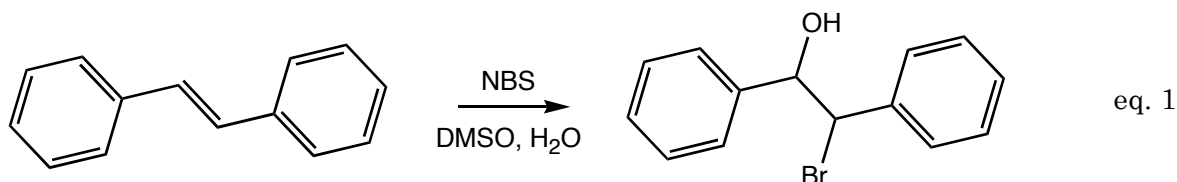
Stereospecificity: Electrophilic Addition and Bromohydrin Formation

Purpose

To perform an electrophilic addition reaction and determine the stereochemical outcome of the reaction.

Background

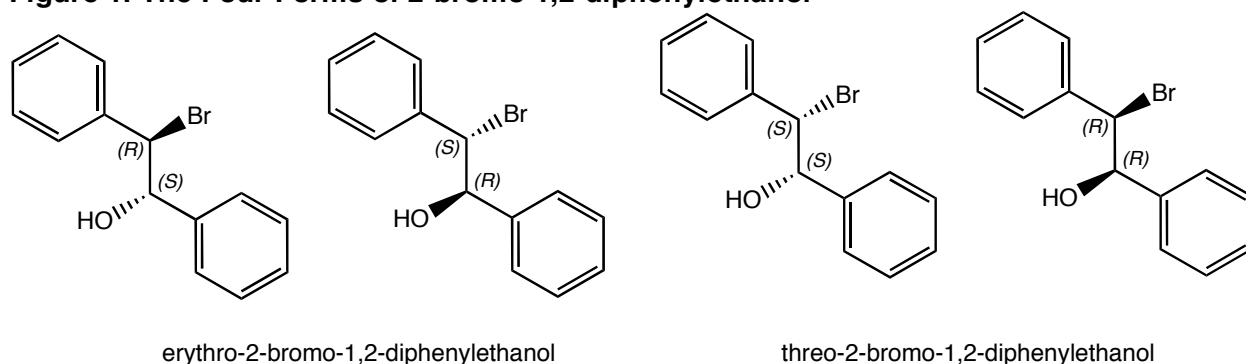
Alkenes are nucleophilic, and as such, they react with electrophiles. The reaction of an alkene with an electrophile occurs in two steps. First, the alkene is attacked by the electrophile and a charged intermediate forms. In the second step, a nucleophile completes the reaction and a stable substituted alkane is formed. For example, bromine and water react with *E*-1,2-diphenylethylene to form 2-bromo-1,2-diphenyl-ethanol (see equation 1).



When the three-dimensional structure of the product is considered, it becomes clear that 2-bromo-1,2-diphenyl-ethanol exists as four distinct molecules, which are in fact a diastereomeric pair of enantiomers. Further, this leads to two significant questions. Which stereoisomers form, and what significance does the product distribution have in terms of the reaction mechanism? For example, if all four stereoisomers form, then the mechanism must be able to account for the formation of four different products. Similarly, if any of the stereoisomers don't form, the mechanism must provide an explanation for both the absence of some stereoisomers and the presence of others.

Since the properties of one enantiomer are the same as the properties of its mirror image, excepting of course the fact that enantiomers interact with polarized light differently, we will only be able to determine which pair of enantiomers is produced by this reaction, the *threo* or *erythro* pair (see figure 1). Since diastereomers have different properties, the *threo* and *erythro* isomers have different melting points, 51–52 °C¹ and 83–84 °C² respectively. Thus, we will be able to identify the product by determining its melting point.

Figure 1. The Four Forms of 2-bromo-1,2-diphenylethanol



Procedure³

Formation of a Bromohydrin

1. Place *trans*-stilbene (*E*-1,2-diphenylethylene) (0.25 g) in a 25-mL Erlenmeyer flask
2. Add water (0.12 mL), dimethylsulfoxide (7 mL), and a stir bar to the flask that contains the *trans*-stilbene.
3. Stir the suspension gently, and if necessary, add a few drops of dimethylsulfoxide, to dissolve the alkene.
4. Add 2 molar equivalents of *N*-bromosuccinimide in equal portions over approximately 5 minutes. (Determine the mass of *N*-bromosuccinimide that should be added *before* coming to lab.)
5. Gently stir the solution for 30 minutes.

Isolation of the Bromohydrin

6. Pour the bright orange solution into a beaker that contains 20 mL of ice-cold water.
7. Add 10 mL of diethyl ether and, using a Buchner funnel, filter the resulting suspension through a pad of celite.
8. Rinse the beaker with 2 mL of diethyl ether, and pour the diethyl ether rinse through the Bucher funnel.
9. Using a separatory funnel, separate the organic and aqueous layers.
10. Extract the aqueous layer with an additional 7 mL of diethyl ether.
11. Combine the organic layers.
12. Using a separatory funnel, wash the combined organic layers with 10 mL of water, and separate the two layers.
11. Wash the combined organic layers again using 10 mL of an aqueous saturated NaCl solution.
12. Remove the salt water and dry the organic layer with anhydrous magnesium sulfate.
13. Remove the magnesium sulfate by filtering the ether–MgSO₄ suspension through filter paper.
14. Using a simple distillation apparatus, remove all but 3 mL of the ether. Transfer the remaining 3 mL of ether to a 5 mL conical vial and evaporate the remaining solvent using a warm water bath and a gentle stream of compressed air.

Recrystallization of the Bromohydrin

15. Recrystallize the bromohydrin from a minimum amount of hot “high-boiling petroleum ether” (5 to 10 mL). Since it is likely that an insoluble solid will be present, carefully add the petroleum ether, and if the solid does not appear to be dissolving either filter or decant the bromohydrin–petroleum ether solution to a second container.
16. Isolate and dry the bromohydrin using a Hirsch funnel.
17. Determine the melting point of the recrystallized bromohydrin.

Report

Draw the reaction of 1,2-diphenylethylene with Br₂ in the presence of water.

Compare the melting points of *erythro*-2-bromo-1,2-diphenylethanol and *threo*-2-bromo-1,2-diphenylethanol to the melting point of your product and determine whether you made the *threo* or *erythro* form of the bromohydrin.

Explain how the formation of a bromonium intermediate, as opposed to a carbocation intermediate, accounts for the products of this reaction.

¹ Dalton, D. R.; Dutta, V. P.; Jones, D. C. *J. Am. Chem. Soc.* **1968**, *90*, 5498.

² Langman, A. W.; Dalton, D. R. *Organic Synthesis* **1980**, *59*, 16.

³ Adapted from Ciaccio, J. A. *J. Chem. Ed.* **1995**, *72*, 1037.